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NASA Technical Memorandum 79188

ELECTROCHEMICAL FLUORINATION
OF TRICHLOROETHYLENE AND
N, N-DIMETHYLTRIFLUOROACETAMIDE

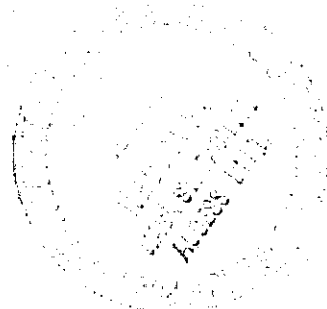
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ELECTROCHEMICAL FLUORINATION OF TRICHLOROETHYLENE AND N, N-DIMETHYLTRIFLUOROACETAMIDE

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ABSTRACT

Fluorination of trichloroethylene and N, N-dimethyltrifluoroacetamide was carried out on a laboratory scale in an advanced "Simons" type electrochemical apparatus which could be operated automatically from ambient to 50 psi pressure. A variety of fluorine-substituted products are formed, depending upon electrolysis conditions and concentrations of reactant relative to the NaF, KF, HF electrolyte. A new reaction mechanism of electrochemical fluorination of trichloroethylene is proposed. The solvency-to-fluorine content relationship of fluorinated N, N-dimethyltrifluoroacetamide is described.

INTRODUCTION

The replacement of hydrogen and/or chlorine with fluorine can impart chemical stability and resistance to oxidation to polymeric materials. It also renders the materials insoluble in common solvents. Specific solvents or special techniques are required to bring them into solution. From the general approximate rule of solubility that "like dissolves like," it is logical to presume that potential solvents for fluorinated polymers may be their relevant fluorinated monomers or oligomers, particularly for those polymers containing functional groups and/or having relatively lower molecular weight.

Electrochemical fluorination is a valuable technique to replace the hydrogen and/or chlorine of a chemical compound with fluorine and at the same time keep certain functional groups intact. The work to be discussed illustrates the use of this technique to fluorinate trichloroethylene (TCE) and N, N-dimethyltrifluoroacetamide (DMTFAA). Our objectives are (1) to study the reaction mechanism of electrochemical fluorination of unsaturated chlorohydrocarbons and (2) to determine the solvency-to-fluorine content relationship of fluorinated DMTFAA (FDMTFAA).

EXPERIMENTAL

Chemicals

Commercial grade anhydrous hydrofluoric acid (AHF) was used either as received or electrochemically dried before introducing the fluorinatable substrate.

Trichloroethylene, fluorocarbon oil (FCO), and halocarbon oil were dried with anhydrous sodium sulfate before use.

N, N-Dimethyltrifluoroacetamide was prepared from N, N-dimethylacetamide (DMAA) and trifluoroacetic anhydride (Ref. 1).

Electrochemical Fluorination Cell

The Simons type cell drawn schematically in Fig. 1 has a capacity of about 300 milliliters. It is constructed from two segments of concentric monel pipes flanged with two pieces of circular Kel-F window plates. The annular space between the pipes serves as a cooling jacket. The cell has twenty two 6.35 by 3.2 by 0.16 centimeters (2.5 by 1.25 by 0.0625 in.) nickel plate electrodes with a total anode area of about 400 square centimeters.

The cell is equipped with a thermocouple, a double-jacket reflux condenser also made of monel, inlets for AHF, liquid and solid substrates, an outlet for draining the reaction products, and a propeller type agitator driven by two sets of magnets. The magnetic stirrer has a hollow shaft through which an inert gas and/or gaseous substrates may be introduced.

The system also includes gas meters, absorbers for effluent gaseous hydrogen fluoride and oxygen fluorides, liquid nitrogen cold traps and a fail-safe device so that the cell can be operated safely at desirable voltages up to 20 volts, temperatures in the range from -45° to about 65° C, and pressures from atmospheric pressure to about 50 psi. A d. c. power source enables electrolysis to be conducted at either a constant voltage or current. And the current may also be periodically reversed by a transistorized automatic reversing switch with two timers.

Cryogenic Analytical Gas-Liquid Chromatograph

The chromatograph is equipped with a thermal-conductivity detector, a liquid nitrogen cooling system, a 10-millivolt chart recorder, and an electronic

digital integrator which automatically counts the retention time of the peak in seconds and calculates the relative peak areas.

Analysis of the fluorinated products were performed by using a 1.8-meter long, 6-millimeter diameter copper tubing column packed with 15% Dow Corning 200 silicone oil on 60/80 mesh Chromosorb W at the oven temperature and helium flowrate designated in the figures. Retention times of the pure compounds involved were obtained separately under corresponding chromatographic conditions.

Spinning Band Distillation Apparatus

The apparatus is composed of a nichrome heated glass column of 10-millimeter diameter and 91-centimeter long, an automatic reflux control device, and a direct bearing-driven stainless steel spiral screen band. The apparatus may be operated for distillation at atmospheric or reduced pressure.

Electrochemical Fluorination of Trichloroethylene (TCE)

Prior to the addition of TCE, the commercial grade AHF with sodium or potassium fluoride in the cell was electrolyzed to remove all traces of moisture. TCE was then introduced with or without a FCO diluent which may also serve as an internal standard for the gas chromatographic analysis of the reaction products. TCE was electrolyzed under the designated conditions for the specified period of time. Samples of the reaction products were freed from hydrogen fluoride by passing them through a column packed with sodium fluoride pellets prior to gas chromatographic analysis.

Table I gives the experimental data for the batches on the electrochemical fluorination of TCE. Batch No. 1 was conducted at constant voltage of about 6 volts. Batch No. 2 at constant current of about 5 amperes. Yields in Table I are calculated from the actual gas chromatographic data as shown in Figs. 2 and 3. No attempt was made to isolate each individual reaction product by fractional distillation.

TABLE I. - ELECTROCHEMICAL FLUORINATION OF
TRICHLOROETHYLENE

	Batch No. 1			Batch No. 2		
	ml	gm	mole	ml	gm	mole
Charge						
TCE	70	102	0.776	117	171	1.30
FCO	125	222	0.555	---	-----	----
AHF	115	115	5.70	190	190	9.75
KF	---	3.5	-----	---	-----	----
NaF	---	-----	-----	---	3.5	----
Reaction conditions						
Cell, °C	5 - 10			0		
Reflux, °C	-35			-40		
N ₂ gas, ml/min	70			120		
Agitation, rpm	1000			2000		
Amperage, DCA	0.8 - 3.7			5		
Voltage, DCV	6			7.5 - 15		
Time, hr	10			4		
Reaction products (B.P., °C) (Ref. 2)						
	gm	mole %		gm	mole %	
CF ₂ ClCF ₂ Cl (3.8)	-----	----		2.4	1.1	
FCO (97.5)	222	48.0		-----	----	
CF ₂ ClCFCl ₂ (47.6)	4.6	2.1		6.3	2.6	
CF ₂ ClCHCl ₂ (71.9)	53.0	27.1		37.2	16.9	
CFHClCFCl ₂ (72.6)	-----	----		1.3	0.6	
TCE (87)	20.4	13.4		121.6	71.2	
CFHClCHCl ₂ (102)	16.5	9.4		15.0	7.6	

Electrochemical Fluorination of N, N-Dimethyltrifluoroacetamide (DMTFAA)

The cell was charged with 140 grams of commercial grade AHF, 2.5 grams each of sodium fluoride and potassium fluoride, 100 milliliters (136 g, 0.965 mole) of DMTFAA, and 60 milliliters (115 g) of a halocarbon oil having an initial boiling temperature of 260°C . Electrolysis was conducted under the following conditions: Nitrogen gas flow rate 100 ml-min^{-1} , agitation speed 2200 rpm, cell temperature 0° to 5°C , reflux condenser temperature -40°C , d.c. voltage 7.5 to 20 volts, and d.c. current 5 to 15 amperes. After 8 hours, about one third of the cell content was drawn out. The cell was brought up to the original volume by adding about 100 milliliters of AHF with an additional 2.5 grams of potassium fluoride. Electrolysis was resumed under nearly the same conditions for another 8 hours. Then about 150 milliliters of the reaction product was removed. Each aliquot after having been freed for the most part from hydrogen fluoride through natural evaporation was neutralized with dilute aqueous NaOH solution. The oily portion which settled out was washed with water and dried with anhydrous sodium sulfate. Gas chromatographic analyses indicated that in the first aliquot (8 hr) about 35% of DMTFAA had converted to FDMTFAA and other byproducts, and the 16-hour one 78% converted.

Reaction products of 35% and 78% DMTFAA conversions were fractionated with a spinning band distillation apparatus at atmospheric pressure. Only portions with boiling temperatures between about 30°C (b.p. of perfluoro DMTFAA) and 130°C (b.p. of DMTFAA) were collected (Ref. 3). About 10 milliliters of FDMTFAA was obtained from the first aliquot and 14 milliliters from the second. No attempt was made to further separate and identify the individual components in these FDMTFAA mixtures. FDMTFAA was used for determining the solubility of a proprietary perfluorinated polyphosphazene elastomer (PFPPE).

Solubility Test of Perfluoropolyphosphazene Elastomer (PFPPE)

The PFPPE sample was ground in a micromill to 200 mesh powder. One gram of PFPPE powder was shaken with 10 milliliter of solvent in a stoppered test tube at room temperature for 8 to 16 hours. Solvents used included DMAA, DMTFAA, FDMTFAA mixtures of 35% and 78% DMTFAA conversions. These results are presented in Table II.

TABLE II. - SOLUBILITY TEST OF
PERFLUOROPOLYPHOSPHAZENE

ELASTOMER

Solvent	Solubility (1 g sample in 10 ml solvent)
DMAA	Immiscible
DMTFAA	A gelatinous interface layer
FDMTFAA, 35% conversion	Miscible, separated after 2 days
FDMTFAA, 78% conversion	A stable slightly hazy homogeneous phase

DISCUSSION

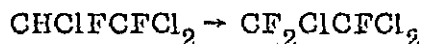
Reaction Mechanism of Electrochemical Fluorination of Trichloroethylene

It has been advocated (Ref. 4) that in the preparation of fluorine containing compounds from unsaturated chlorohydrocarbons such as TCE by electrolysis in liquid AHF at about 0° C and 6 volts, the following stepwise reactions are involved:

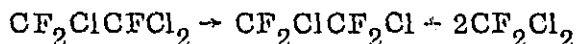
Step 1. Addition of fluorine to the double bond



Step 2. Replacement of hydrogen with fluorine



Step 3. Further fluorination reactions

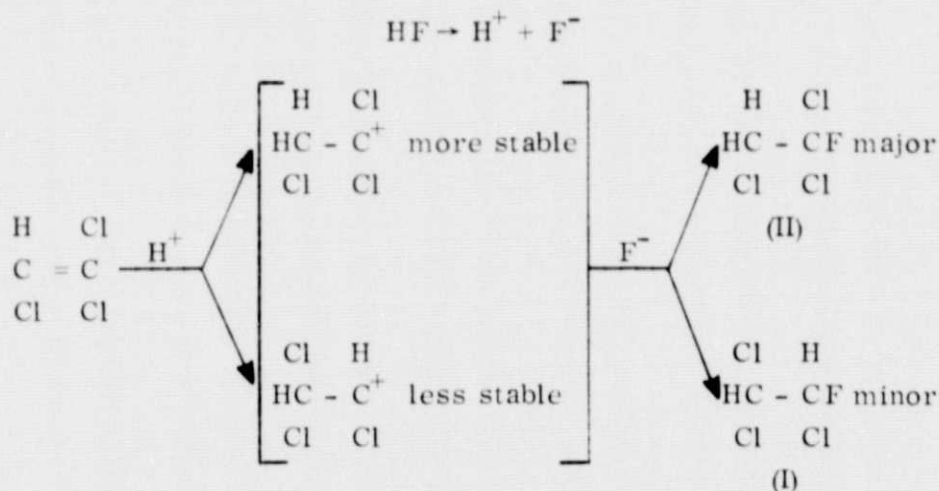


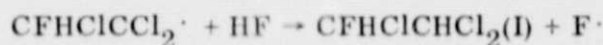
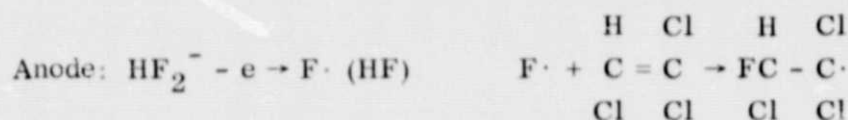
Our results indicate that the primary step of electrochemical fluorination of TCE is hydrogen fluoride addition to the double bond rather than fluorine addition. Furthermore, the addition of hydrogen fluoride to TCE is homolytic rather than heterolytic in nature. Figure 4 is a schematic diagram postulating routes of formation and possible reaction products involved in the electrochemical fluorination of TCE. Whereas in Figs. 5 and 6, actual reaction products with their relative yields found from our experiments are listed. From Figs. 5 and 6, one notes that substantial amounts of compound (I), indicative of HF addition, were found among the reaction products of both batches.

The presence of a small amount of compound (IV) in Batch No. 2 most likely results from the replacement of hydrogen of compound (I) with fluorine

rather than the addition of fluorine to TCE. If compound (IV) is formed by the addition of fluorine to TCE, it should be present in both batches and in substantial amounts. Since the reaction condition of Batch No. 2 is relatively more drastic (7.5 to 15 v and without diluent) than that of Batch No. 1 (6 v and with diluent), the presence of a small amount of compound (IV) in Batch No. 2 but not in Batch No. 1 can be rationalized.

The absence of compound (II) among the reaction products of both batches indicates that the addition of HF to TCE is not heterolytic but homolytic in nature. A heterolytic reaction mechanism of the addition of HF to TCE, $\text{CHCl} = \text{CCl}_2$, would be similar to that of HCl to $\text{CH}_2 = \text{CHBr}$. The addition of HCl to $\text{CH}_2 = \text{CHBr}$ proceeds through the carbonium ion, CH_3CHBr^+ , to give CH_3CHBrCl , rather than through $^+\text{CH}_2\text{CH}_2\text{Br}$, which would give $\text{CH}_2\text{ClCH}_2\text{Br}$ (Ref. 5). Similarly, the heterolytic addition of HF to $\text{CHCl} = \text{CCl}_2$ would proceed through the carbonium ion, $\text{CH}_2\text{ClCCl}_2^+$, to give $\text{CH}_2\text{ClCFCl}_2$ (II), rather than through $^+\text{CHClCHCl}_2$ which would give CHFCICHCl_2 (I). Since what we found from the reaction products of both batches is compound (I) not compound (II), a heterolytic reaction mechanism on the addition of HF to TCE such as the following may be ruled out.

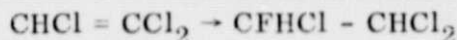




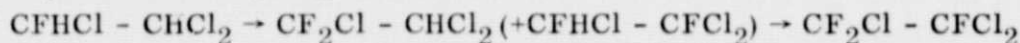
The homolytic addition of HF to TCE, $\text{CHCl}=\text{CCl}_2$, will proceed through the intermediate free radical, $\text{CFHClCCl}_2 \cdot$, to give $\text{CFHClCHCl}_2(\text{I})$, rather than through $\cdot\text{CHClCFCl}_2$ which would give $\text{CH}_2\text{ClCFCl}_2(\text{II})$. Not only is the intermediate free radical $\text{CFHClCCl}_2 \cdot$ more stable than $\cdot\text{CHClCFCl}_2$, the steric hindrance arising from two chlorine atoms on the same carbon will inhibit the $\text{F} \cdot$ radical from approaching to the reaction site to form the intermediate free radical, $\cdot\text{CHClCFCl}_2$. We believe that is why we found compound (I) not compound (II) in the reaction products of both batches.

Therefore, from our experimental results and above discussion, we conclude that in the electrochemical fluorination of unsaturated chlorohydrocarbons such as TCE in liquid AHF medium and under moderate reaction conditions, the following stepwise reactions are involved:

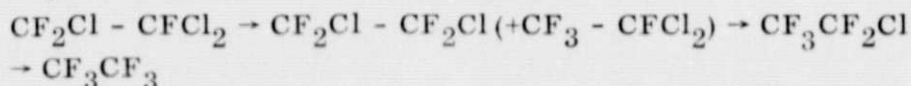
Step 1. Homolytic addition of hydrogen fluoride to the double bond



Step 2. Replacement of hydrogen with fluorine



Step 3. Replacement of chlorine with fluorine



The fluorinated products that may result from the cleavage of carbon to carbon bond are not considered.

Solvency-to-Fluorine Content Relationship of Fluorinated

N, N-Dimethyltrifluoroacetamide (FDMTFAA)

The solubility of a substance is a measure of equilibrium between the intermolecular forces in the pure solute and the solvent-solute interactions. The forces vary greatly with the composition, structure, and size of solute and solvent molecules. In general, increased structural similarity between solute and solvent is accompanied by increased solubility. For polymers, an increase in molecular weight alone usually leads to a decrease in solubility. For example, polytetrafluoro-

ethylene with a molecular weight in the millions does not dissolve in any available solvents including fluorocarbon oils.

Partially fluorinated poly (organophosphazenes) were reported soluble in trichlorotrifluoroethane, dimethylformide, etc. (Ref. 6). Potential solvents for perfluoropolyphosphazenes are probably fluorinated nitrogen or phosphorous compounds. Our preliminary solubility test of a PFPPE with DMAA and DMTFAA (Table II) showed that the fluorinated polymer is completely immiscible with DMAA but forms a gelatinous interfacial layer with DMTFAA. This phenomenon of intermolecular attraction between solute and solvent apparently is attributed to the fluorine atoms in DMTFAA. The solvency of DMTFAA may be further increased by increasing its fluorine content. To test this the electrochemical fluorination of DMTFAA to 35% and 78% of conversion was carried out so that the fluorinated DMTFAA would have different fluorine contents. Our solvency study of these two FDMTFAA's (Table II) shows that the fluorinated polymer can be dispersed in both FDMTFAA samples with differing degrees of stability. The dispersion prepared from PFPPE and FDMTFAA at 35% conversion separates into two layers after standing for 2 days, whereas that from PFPPE and FDMTFAA at 78% conversion appears to be as stable as a true solution. We assume that the FDMTFAA of 78% conversion not only contains more fluorine than that of 35% conversion, but both of its two N-methyl groups must be fluorinated to some degree so that the solute-solvent interaction forces are strong enough to prevent solute-solvent from separation. From the solvency-to-fluorine content relationship observed in this study, we conclude that an increase in fluorine content of DMAA is accompanied with increased solvency as illustrated below.

FDMTFAA, 78% conversion > FDMTFAA, 35% conversion > DMTFAA >> DMAA. However, in order to dissolve the fluorinated polymer, all the three methyl groups of DMAA have to be fluorinated to some degree so that the solvent molecule can intermingle with the fluorinated polymer in all orientations.

CONCLUSIONS

Our investigation on electrochemical fluorination of trichloroethylene and N, N-dimethyltrifluoroacetamide leads us to the following conclusions:

1. Electrochemical fluorination is a useful method of synthesizing fluorinated solvents.

2. Electrochemical fluorination allows a step-by-step controlled fluorination. This technique is useful for studying reaction mechanism of fluorinating organic compounds.
3. Fluorinated solvents show a higher degree of solvency for fluorinated polymers than their corresponding unfluorinated ones.

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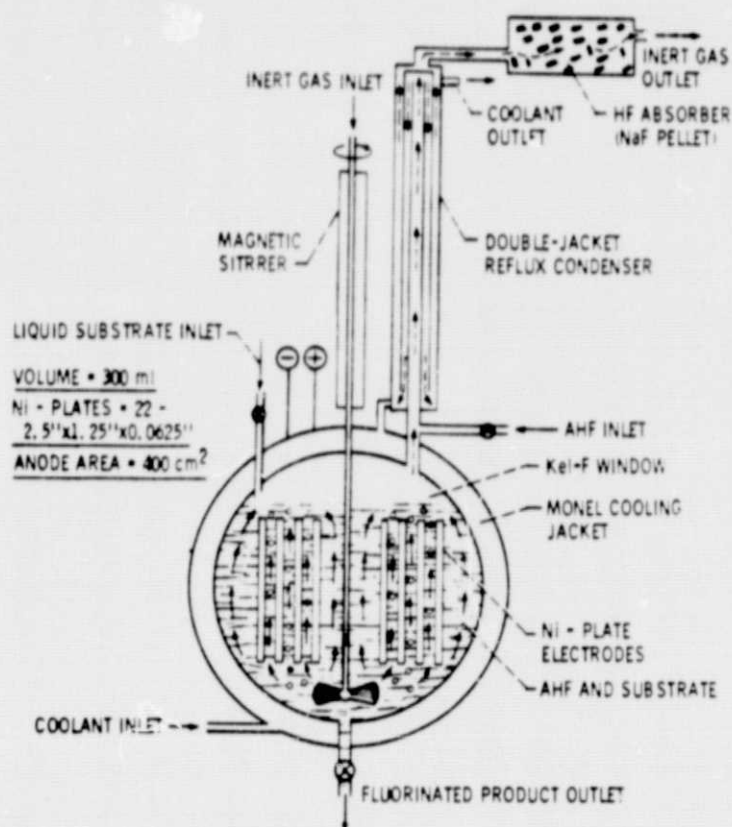


Figure 1. - Electrochemical fluorination apparatus.

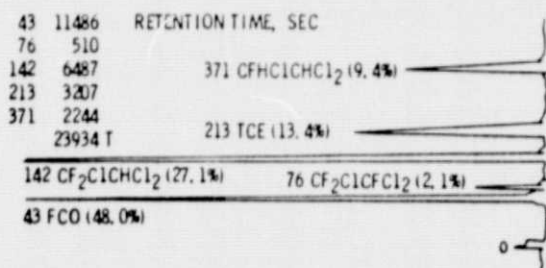


Figure 2. - Gas chromatographic analysis of the reaction products of electrochemical fluorination of trichloroethylene, Batch no. 1. Oven temperature 70° C, helium flowrate 70 ml min⁻¹, approximate retention times of the pure compounds: FCO 44, TCE 213, CFHClCHCl₂ 370.

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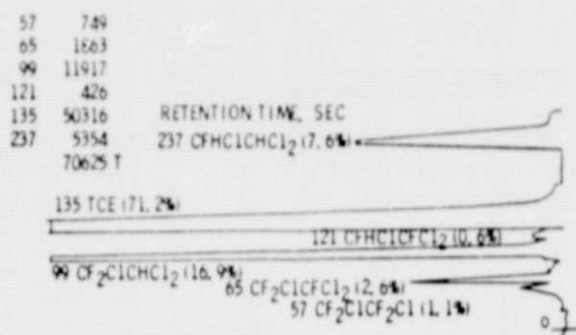


Figure 3. - Gas chromatographic analysis of the reaction product of electrochemical fluorination of trichloroethylene, Batch no. 2. Oven temperature 90° C, helium flowrate 70 ml min⁻¹, approximate retention times of the pure compounds: TCE 134, CFHC1CHC1₂ 237.

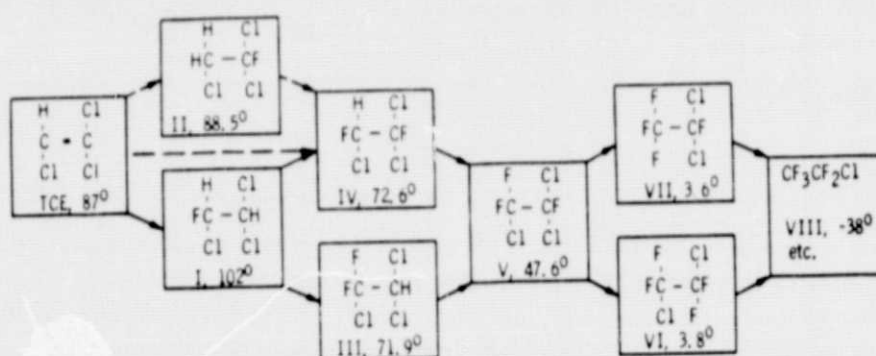


Figure 4. - Prospective reaction products of electrochemical fluorination of trichloroethylene.

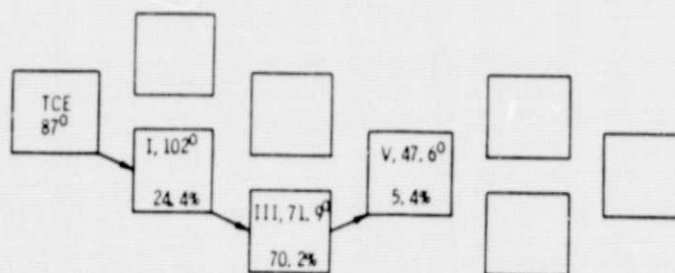


Figure 5. - Relative yields of the reaction products of electrochemical fluorination of trichloroethylene, Batch no. 1 (74.2% of conversion).

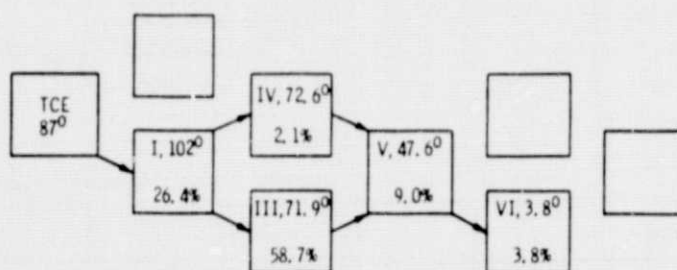


Figure 6. - Relative yields of the reaction products of electrochemical fluorination of trichloroethylene, Batch no. 2 (28.8% of conversion).